

Formation of a Donor-Stabilized Tetrasilacyclobutadiene Dication by a Lewis Acid Assisted Reaction of an *N*-Heterocyclic Chloro Silylene

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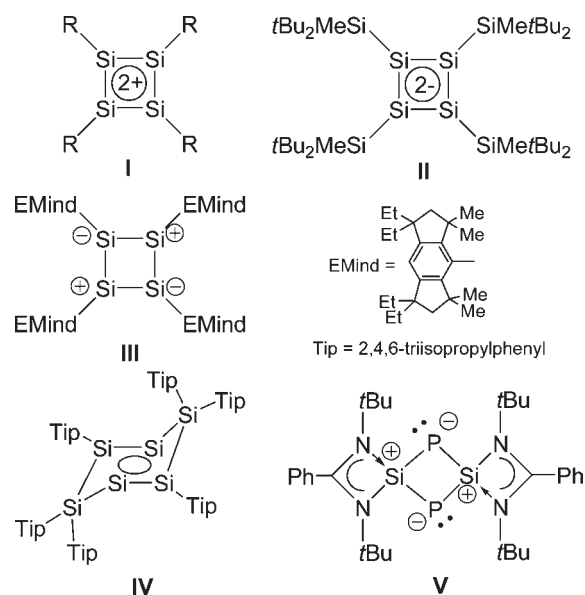
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Supporting Information

ABSTRACT: The first donor-stabilized tetrasilacyclobutadiene dication species has been synthesized and fully characterized. Its unexpected formation occurs by the Lewis acid assisted reaction of the *N*-heterocyclic chloro silylene [L(Si:Cl)] (L = PhC(N*t*Bu)₂; amidinate) with Cp*ZrCl₃ (Cp* = pentamethylcyclopentadienyl) in the molar ratio of 3:2. Remarkably, the four-membered Si₄ core consists of two *N*-donor stabilized silylium subunits and two silylene-like moieties. The dicationic charge is somewhat delocalized on the Si₄ core, which is supported by DFT calculations.

The synthesis and isolation of reactive intermediates in main group chemistry provides important insight into the geometrical and electronic structure of elusive species and gives important clues to their reactivity.¹ In particular, silylium ions have been of significant interest to a wide range of chemists because of their interesting properties and the significant differences compared to carbenium ions.^{2,3} The challenge of synthesizing ‘free’ stable silylium ions has been accomplished using several techniques.^{4,5} However, the isolation and structural characterization of a larger variety of silylium ions, in particular polynuclear silylium ions,^{4c,e,g,i} deserves great attention owing to their potential in catalysis⁶ and use as building blocks in silicon chemistry.^{1,2} Among polynuclear silylium ions, tetrasilacyclobutadiene dication derivatives **I** are of interest from both a fundamental and synthetic point of view but elusive until now (Scheme 1). In view of the dicationic charge of the cyclo-Si₄ core of **I**, its geometric and electronic structure is of particular interest. In contrast to dications **I**, the tetrasilacyclobutadiene dianion **II** has been successfully synthesized by Sekiguchi and co-workers (Scheme 1).⁷ Interestingly, **II** has a puckered dianionic Si₄ ring and lacks a diatropic ring current. Very recently, Tamao and co-workers reported the isolation of neutral tetrasilacyclobutadiene **III** with a ylide-like Si₄ ring, which disfavors 4π-electron delocalization and thus no ring current can be obtained (Scheme 1).⁸ A somewhat related and unique unsaturated Si system containing a π-electron delocalized Si₄ subunit represents the hexasilabenzene isomer **IV**.⁹ Furthermore, the synthesis of a zwitterionic 2,4-disila-1,3-diphosphacyclobutadiene **V** stabilized with an amidinate ligand L [L = PhC(N*t*Bu)₂] has recently been reported independently by ourselves and Roesky’s group (Scheme 1).¹⁰ This result demonstrates the ability of amidinate ligands to stabilize unsaturated silylium-like moieties in small ring

Scheme 1. Tetrasilacyclobutadiene Dication **I**, Tetrasilacyclobutadiene Dianion **II**, Tetrasilacyclobutadiene **III**, Hexasilabenzene Isomer **IV**, and 2,4-Disila-1,3-diphosphacyclobuta-1,3-diene **V**



compounds. In this communication, we report the remarkable formation of the first amidinato-stabilized cyclo-Si₄ dication, bearing, in addition, two terminal chloro silylene donors.

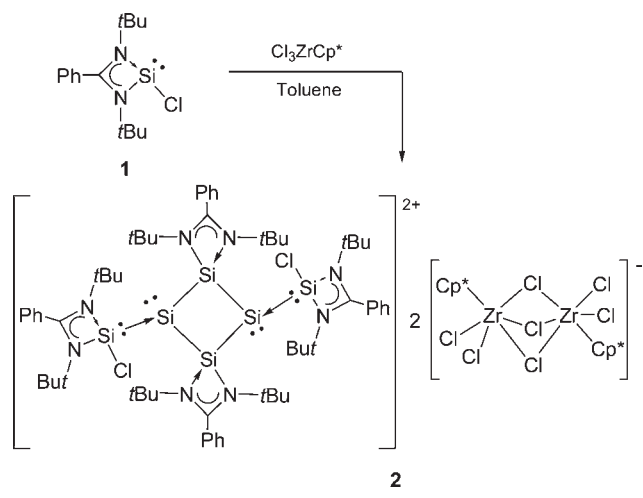
The reaction of *N*-heterocyclic chloro silylene LSiCl¹¹ **1** with pentamethylcyclopentadienyl zirconium trichloride Cl₃ZrCp* (Cp* = C₅Me₅) in the molar ratio of 3:2 in toluene at room temperature resulted in the formation of the unexpected unique compound **2**, which could be isolated as yellow crystals in 29% yield and was fully characterized by NMR spectroscopy and X-ray analysis (Scheme 2). When a different molar ratio of starting materials was used (1:1, 2:1, and 3:1), significantly smaller yields were obtained. While compound **2** exhibits low solubility in hydrocarbon solvents, it is soluble in dichloromethane. However, compound **2** slowly undergoes decomposition in dichloromethane solutions over two days to give a complex mixture, including LSiCl₃¹² and unidentified compounds.

The formation of compound **2** is also astonishing with respect to the results reported by Dias and co-workers who

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Scheme 2. Synthesis of 2



showed that germyliumylidene and stanniumylidene cations $[\text{L}'\text{E}]^+[\text{Zr}_2\text{Cl}_7\text{Cp}_2]^-$ ($\text{E} = \text{Ge}(\text{II}), \text{Sn}(\text{II})$; $\text{L}' = N$ -isopropyl-2-(isopropylamino)troponimine) can be synthesized upon the reaction of cyclopentadienyl zirconium trichloride Cl_3ZrCp with chloro germylene and stannylene analogues $[\text{L}'\text{ECl}]$, respectively.¹³ Although the reaction mechanism for the formation of compound 2 is unknown as yet, we propose that the initial step of this reaction is a chloride abstraction from 1 by 2 molar equiv of the Lewis acid Cp^*ZrCl_3 to form the transient silyliumylidene cation in $[\text{LSi}]^+[\text{Zr}_2\text{Cl}_7\text{Cp}_2]^-$ 3. Subsequently, the latter highly electrophilic LSi^+ cation undergoes a disproportionation reaction, resulting in the formation of 2, LH^+Cl^- (ESI-MS) LSiCl_3 , and other yet unidentified products. This suggests that the stability of a silyliumylidene cation is strongly dependent on the nature of the counteranion. In fact, stable silyliumylidene cations are scarce but could be isolated by taking advantage of the $\text{B}(\text{C}_6\text{F}_5)_4$ counteranion.⁵ However, our attempts to stabilize the proposed LSi^+ cation through addition of $\text{LiB}(\text{C}_6\text{F}_5)_4$ to the mixture of 1 and Cp^*ZrCl_3 were hitherto unsuccessful.

The molecular structure of 2 has been determined by NMR spectroscopy and X-ray diffraction analysis (Figure 1). The planar Si_4 core has a rhombus shape (the sum of the internal bond angles is 360.0°). Accordingly, endocyclic $\text{Si}3-\text{Si}2-\text{Si}3^*$ and $\text{Si}2-\text{Si}3-\text{Si}2^*$ angles are $98.85(7)^\circ$ and $81.15(7)^\circ$, respectively. The cationic silicon atoms ($\text{Si}2$ and $\text{Si}2^*$) of the Si_4 ring in 2 are stabilized by amidinato ligands, which are oriented almost perpendicularly to the Si_4 plane, whereas the bis-silyl silylene centers ($\text{Si}2$ and $\text{Si}2^*$) are coordinated by a chloro silylene moiety $[\text{L}(\text{Si})\text{Cl}]$. The position of the LSiCl groups on the $\text{Si}3$ and $\text{Si}3^*$ atoms deviate above and below the Si_4 ring plane $[65.87(10)^\circ]$. This is also evident by measuring the sum of the bond angles at $\text{Si}3$ and $\text{Si}3^*$ (312.03°). The $\text{Si}2-\text{Si}3$ and $\text{Si}2-\text{Si}3^*$ bond lengths of 2 (2.321(2) and 2.331(2) Å) are similar to that of the ion-separated tetrasilacyclobutadiene dianion II (2.2989(8), 2.3300(8), 2.3576(8), and 2.3301(8) Å: average of 2.3292 Å),⁷ and somewhat longer than that of tetrasilacyclobutadiene III (2.2877(8), 2.2924(8), 2.2671(8), and 2.2846(8) Å: average of 2.2830 Å).⁸ Furthermore, the skeletal $\text{Si}-\text{Si}$ bond lengths of the dication of 2 are comparable to the $\text{Si}-\text{Si}$ bond lengths in the central aromatic four-membered ring subunit of the hexasilabenzene isomer IV (Scheme 1) (2.3275(5) and 2.3034(8) Å).⁹

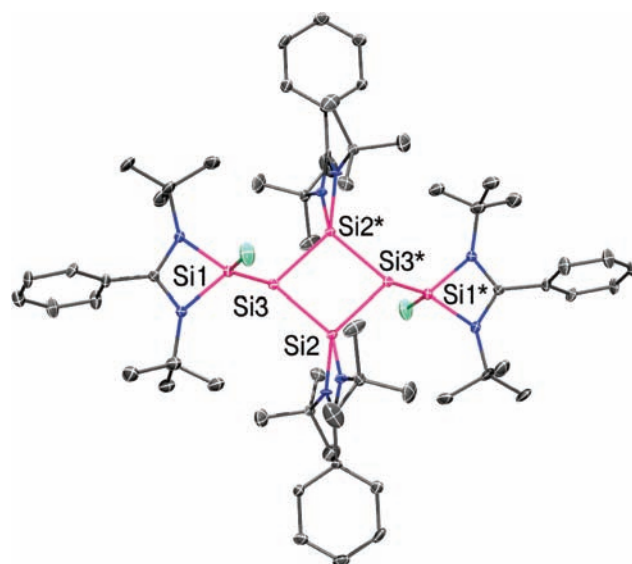


Figure 1. Molecular structure of the dication of 2. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: $\text{Si}1-\text{Si}3$ 2.3044(19), $\text{Si}2-\text{Si}3$ 2.321(2), $\text{Si}2-\text{Si}3^*$ 2.331(2), $\text{Si}2-\text{Si}3-\text{Si}2^*$ 81.15(7), $\text{Si}3-\text{Si}2-\text{Si}3^*$ 98.85(7).

Interestingly, the $\text{Si}1-\text{Si}3$ distance in 2 [2.3044(19) Å] is shorter than that of the skeletal $\text{Si}-\text{Si}$ bond lengths in 2 and typical $\text{Si}-\text{Si}$ single bonds (2.34 Å),¹⁴ implying a strong $\text{Si}1\rightarrow\text{Si}3$ donor-acceptor interaction of the LSiCl ligand ($\text{Si}1$ lone pair) to the silylene-like Si ring atom ($\text{Si}3$). Moreover, the trans-annular separations are 3.026 Å for $\text{Si}2\cdots\text{Si}2^*$ and 3.534 Å for $\text{Si}3\cdots\text{Si}3^*$, both of which are shorter than the van der Waals radii of Si (4.20 Å).

The ^{29}Si NMR spectrum of freshly prepared solutions of 2 in CD_2Cl_2 shows three signals at $\delta = -128.7$ ($\text{Si}3-\text{Si}$), 7.7 ($\text{LSi}1\text{Cl}$), and 53.4 ppm ($\text{LSi}2-\text{Si}$), respectively. The GIAO calculations of 2 [GIAO/B3LYP/6-311(d) for (H, C, N, Cl), 6-311G(3d) and for (Si)//B3LYP/6-31G(d)] is in good agreement with the experimental data and confirmed the assignment (-101.0 , 19.8, and 67.7). As expected, the chemical shift of the four-coordinate cationic silicon atom ($\text{Si}2$) is upfield shifted in comparison to those of silyl cations with three-coordinate silicon due to the nitrogen donor of the amidinato ligand and the electropositive silicon atoms bound to the cationic $\text{Si}2$ center.³⁻⁵ The δ value of the silylene center ($\text{Si}3$) is also significantly shifted to higher field in comparison to those reported for silylenes with two-coordinate silicon owing to the LSiCl donor coordination.¹⁵ Consistently, the solid-state ^{29}Si NMR spectrum of 2 reveals three singlet signals at $\delta = -124.8$ ($:\text{Si}3-\text{Si}$), 10.7 ($\text{LSi}1\text{Cl}$), and 53.9 ($\text{LSi}2-\text{Si}$) ppm, which are almost identical with the ^{29}Si NMR spectrum in CD_2Cl_2 solutions and reflects that the ion pair 2 retains its structure in solution.

In order to understand the electronic nature of the dication of 2, we performed quantum chemical calculations using density functional theory at the B3LYP/6-31G(d) level. The structural parameters obtained by X-ray crystallographic analysis (the counteranions were omitted) were used as the initial structure.¹⁶ The optimized geometry of 2 closely reproduced the experimental data (see Supporting Information). The LUMO of 2 shows $3p-3p$ orbital interaction between the cationic silyl moieties in the Si_4 ring (Figure 2a). The HOMO and HOMO-1 of 2 (Figure 2b and c) represent degenerate orbitals consisting of

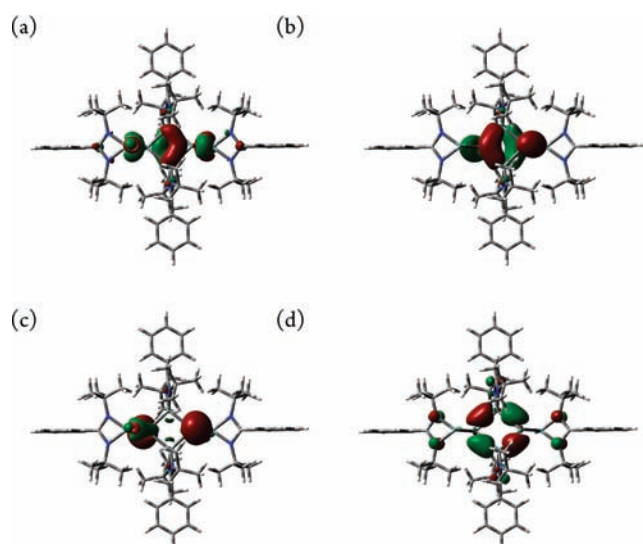
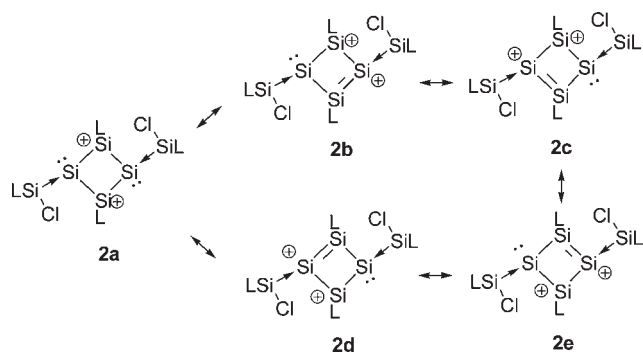


Figure 2. Molecular orbitals of **2'** representing the presence of p–p interaction (LUMO, a), lone-pair orbitals of the silylene center (Si3 and Si3*) (b and c), and σ -bonding orbitals within the Si₄ ring (d): LUMO (a), HOMO (b), HOMO–1 (c), and HOMO–2 (d).

Scheme 3. Resonance Structures of **2**



a lone pair orbital at the silylene center (Si3 and Si3*) and dative bonding orbitals (Si1→Si3 and Si1*→Si3*). The HOMO–2 of **2** represents primarily the Si–Si σ bonding orbitals of the Si₄ core (Figure 2d). Consistent with the experimental results and the donor–acceptor concept, the natural population analysis (NPA) charges of the silylene-like (acceptor) Si centers of the Si₄ ring (Si3 and Si3*) bear negative net charges (–0.494); on the other hand, the four-coordinate silylium-like Si atoms (Si2 and Si2*) have positive charges (+1.056). Furthermore, NBO analysis of **2** reveals that the Si₄ core has four occupied σ bond orbitals for the Si–Si bonds (1.644e for Si2–Si3, 1.621e for Si2–Si3*, 1.706e for Si2*–Si3, and 1.781e for Si2*–Si3*) as well as two filled lone pair orbitals with 1.684 electrons on the Si3 and Si3* atoms. This σ -bonding character in the Si₄ ring of **2** is also supported by the WBI (Wiberg Bond Index) values [1.045 for Si2–Si3, 1.046 for Si2*–Si3*, and 1.044 for both Si2*–Si3 and Si2–Si3*]. Interestingly, the nucleus independent chemical shift (NICS)¹⁷ of **2** revealed negative values [NICS(1) = –3.8 and NICS(0) = –4.7 ppm], indicating that **2** has a aromatic ring current by the delocalization of π -electrons. This is in contrast to the tetrasilacyclobutadiene dianion **II** and tetrasilacyclobutadiene **III** which are antiaromatic.^{7,8} Judging from all experimental and

theoretical results, compound **2** is best depicted by the charge localized resonance structure **2a** with some contribution from the π -electron delocalized aromatic resonance form represented by **2b–e** (Scheme 3). This aromatic character of **2** is similar to that observed for the isoelectronic zwitterionic 2,4-disila-1,3-diphosphacyclobutadiene **V**.¹⁰ Both isoelectronic compounds **2** and **V** have amidinato ligands on the skeletal Si atoms, indicating that the amidinato ligand leads to the unique character of the unsaturated silicon four-membered system.

In conclusion, we have reported the synthesis and isolation of the first donor-stabilized tetrasilacyclobutadiene dication of **2** by an unexpectedly simple procedure. Compound **2** represents a novel type of silylium(ylidene)-like cation as well as a new unsaturated type of four-membered silicon ring system. The use of compound **2** as a precursor for transition-metal π -complexes bearing a dicationic π -conjugated cyclo-Si₄ ring system is currently in progress.

ASSOCIATED CONTENT

S Supporting Information. Experimental details including spectroscopic data, CIF files and DFT computational details for compounds **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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